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(54) Title: LUBRICANT COMPOSITIONS FOR AND THEIR USE IN INTERNAL COMBUSTION ENGINES (57) Abstract A low phosphorus lubricant containing a metallocene-catalysed polymer-based dispersant and at least one of copper and molybdenum provides fuel economy with maintained wear and oxidation protection.		

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LUBRICANT COMPOSITIONS FOR AND THEIR USE IN INTERNAL COMBUSTION ENGINES

This invention relates to lubricating compositions, especially crankcase lubricants for internal combustion engines, more especially those for use in road vehicles. It relates in particular to compositions which lead to improved fuel economy, and especially to compositions that do so while maintaining the antiwear performance of the lubricating composition, its resistance to oxidation, or both.

International Application WO 96/06904 describes a lubricant comprising a molybdenum compound, a zinc dialkyldithiophosphate (hereinafter ZDDP), a sulphur compound, an ashless dispersant, and a boron compound. The ashless dispersant is advantageously a reaction product of a polyisobutylene succinic acid with a polyamine, and this may be borated to combine the ashless dispersant with the boron compound. An alternative backbone for the ashless dispersant is an ethylene- α -olefin copolymer. The sulphur compound may be, for example, a copper, zinc, or nickel dialkyldithiocarbamate. The lubricant gives sustained fuel economy.

EP-A-770 668 describes a lubricant containing ZDDP, a copper carboxylate, and a molybdenum salt, optionally together with an optionally borated ashless dispersant, alkenylsuccinimides being given as examples of the latter. The lubricant is said to retain its friction-reducing properties after long use.

EP-A-353 935 describes the use in a lubricating oil composition of an ashless dispersant derived from an ethylene- α -olefin copolymer obtained by metallocene/alumoxane catalysed polymerization, the copolymer being characterized by having at least 30% terminal ethenylidene unsaturation. The dispersant is obtained by reaction with an ethylenically unsaturated acid or anhydride, e.g., maleic anhydride, and

the resulting acidic groups reacted with, for example, a polyamine. The composition may contain, *inter alia*, ZDDP and copper and molybdenum compounds.

While the use of ZDDP's or other dihydrocarbyl dithiophosphate salts as anti-wear agents and antioxidants is common, it has been found that the phosphorus in such materials has a harmful effect on catalytic converters and for this and other reasons it is desirable to minimize the proportions of such materials so far as possible consistent with maintaining the desired properties of the lubricating composition.

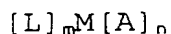
The present invention provides a lubricant composition comprising a lubricating base stock, a dispersant, a metal dihydrocarbyl dithiophosphate, and either a copper-containing compound or a molybdenum-containing compound, the composition comprising at most 0.1% by weight of phosphorus, and the dispersant comprising a hydrocarbon polymer carrying a functional group, the polymer comprising monomeric units derived from ethylene and from at least one α -olefin having from 3 to 16 carbon atoms, ethylene-derived units representing from 1 to 50% by weight of the polymer, the number average molecular weight of the polymer being from 1500 to 10000, and at least 30% of the polymer chains having terminal ethenylidene unsaturation before reaction to add the functional group.

Advantageously, the phosphorus content of the composition is at most 0.08% and preferably it is at most 0.06%, more preferably at most 0.05%, by weight of the composition.

Advantageously the α -olefin from which the hydrocarbon polymer of the dispersant is derived is an alkene, preferably propene or butene (iso- or, preferably, n-). Advantageously the ethylene content is from 15 to 50%, preferably 20 to 40%, by weight of the polymer. Advantageously, the molecular

weight of the polymer is from 1500 to 4500, preferably from 1800 to 3500. The molecular weight may be measured by gel permeation chromatography.

As used herein, the term "terminal unsaturation" is the unsaturation provided by the last monomer unit located in the polymer. Advantageously at least 50%, and preferably at least 60%, and most preferably from 75 to 95%, of the polymer chains contain terminal ethenylidene unsaturation. The above-mentioned EP-A-353 935 describes a process for the manufacture of such polymers, and processes by which they may be provided with functional groups, and its entire disclosure is incorporated by reference herein. The polymers may be prepared by various polymerization processes using metallocene catalysts which are, for example, bulky ligand transition metal compounds of the formula:



where L is a bulky ligand; A is a leaving group, M is a transition metal, and m and n are such that the total ligand valency corresponds to the transition metal valency. Preferably the catalyst is four co-ordinate such that the compound is ionizable to a 1⁺ valency state.

The ligands L and A may be bridged to each other and if two ligands A and/or L are present they may be bridged. The metallocene compound may be a full sandwich compound having two or more ligands L which may be cyclopentadienyl ligands or cyclopentadienyl-derived ligands, or they may be half sandwich compounds having one such ligand L. The ligand may be mono- or polynuclear or any other ligand capable of appropriate bonding to the transition metal, which may be one or more Group 4, 5 or 6 transition, lanthanide or actinide metals, with zirconium, titanium and hafnium being particularly preferred.

The ligands may be substituted or unsubstituted, and mono-, di-, tri-, tetra- and penta-substitutions of the cyclopentadienyl ring are possible. Optionally the substituent(s) may act as one or more bridges between the
5 ligands and/or leaving groups and/or transition metal. Such bridges typically comprise one or more of a carbon, germanium, silicon, phosphorus or nitrogen atom-containing radical, and preferably the bridge places a one atom link between the entities being bridged, although that atom may
10 and often does carry other substituents.

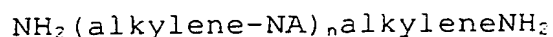
The metallocene may also contain a further displaceable ligand, preferably displaced by a cocatalyst - a leaving group - that is usually selected from a wide variety of hydrocarbyl groups and halogens.

15 Such polymerizations, catalysts, and cocatalysts or activators are described, for example, in U.S. Patents Nos. 4 530 914, 4 665 208, 4 808 561, 4 871 705, 4 897 455, 4 937 299, 4 952 716, 5 017 714, 5 055 438, 5 057 475, 5 064 802, 5 096 867, 5 120 867, 5 124 418, 5 153 157,
20 5 198 401, 5 227 440 and 5 241 025; EP-A-129 368, 277 003, 227 004, 420 436 and 520 732; and WO 91/04257, 92/00333, 93/08199, 93/08221, 94/07928 and 94/13715, the disclosures of all of which are incorporated herein by reference.

The oil soluble polymeric hydrocarbon backbone may be
25 functionalized to incorporate a functional group into the backbone of the polymer, or as one or more groups pendant from the polymer backbone. The functional group typically will be polar and contain one or more hetero atoms such as P, O, S, N, B or Hal. It may be attached to a saturated
30 hydrocarbon part of the oil soluble polymeric hydrocarbon backbone by a substitution reaction or to an olefinic portion by an addition or cycloaddition reaction. Alternatively, the functional group may be incorporated into the polymer in

conjunction with oxidation or cleavage of the polymer chain end (e.g., as in ozonolysis).

As preferred examples of providing functionality, there may be mentioned more especially the "ene" reaction with
5 unsaturated mono or dicarboxylic acids or anhydrides, especially maleic anhydride, followed by reaction of the carboxylic group or groups with a nucleophilic reactant, for example, an alcohol, including a polyol, aminoalcohol, reactive metal compound or, especially, an amine, preferably
10 a polyamine. As polyamine, there is advantageously used an alkylene polyamine, including a polyalkylene polyamine, for example a compound of the formula



15

wherein A represents hydrogen or an alkyl group, advantageously one with at most three carbon atoms, and n has an average value of from 1 to 10, preferably at least 3, and more preferably from 3 to 6. The alkylene group is
20 advantageously ethylene.

Functionality may be provided by other means, for example, by oxidation, hydroformylation, epoxidation, reaction with a hydroxyaromatic compound or by the Koch reaction. Provision of functionality by the Koch reaction is
25 described in International Application No. WO 94/13709, the entire disclosure of which is incorporated herein by reference. According to the procedure described in the International Application, a terminal ethenylidene group is treated with carbon monoxide in the presence of an acid
30 catalyst and a nucleophilic trapping agent, and the resulting acidic group subsequently treated, as described above, by a nucleophilic reactant, the preferred reactant being a polyamine, and most preferably one of the formula given above.

The resultant dispersant may be post-treated with further reactants, for example, urea, thiourea, carbon disulphide, aldehydes, ketones, carboxylic acids or anhydrides, nitrides, epoxides, phosphorus compounds or, more especially, boron compounds. The preferred amine-terminated ashless dispersant is preferably treated with, for example, a boron oxide, acid, or halide to provide a borated dispersant which advantageously contains from 0.05 to 2.0, preferably 0.05 to 0.7, % by weight boron.

10 The dispersant is advantageously present in a proportion of 0.1 to 20, preferably 1 to 8, % by weight of the composition.

The base stock may comprise natural or synthetic oils, or mixtures of natural and synthetic oils. As synthetic base stock there may be mentioned esters, especially alkyl esters of mono and polycarboxylic acids, monocarboxylic esters of polyols, and complex esters, poly α -olefins, including polybutenes, alkylbenzenes, phosphate esters and polysilicone oils. Natural base stocks, within Groups I, II, and III of the API EOLCS 1509 definition, include mineral lubricating oils which may vary widely as to their crude source, for example, as to whether they are paraffinic, naphthenic, mixed, or paraffinic-naphthenic, as well as to the method used in their production, for example, their distillation range and whether they are straight run or cracked, hydrofined, or solvent extracted. Also used may be Group IV and Group V base stocks.

The lubricating oil base stock mixture conveniently has a viscosity of 2 to 50, advantageously 2.5 to 12, cSt, or 30 mm^2/s , and preferably 3.5 to 9 cSt., or mm^2/s , at 100°C, the actual value depending on the lubricant grade being manufactured.

As metal dihydrocarbyl dithiophosphates, there may be mentioned more especially those where the metals are alkali

metals, alkaline earth metals, magnesium, aluminium, lead, tin, molybdenum, manganese, nickel, copper and, advantageously, zinc.

The compound may advantageously be employed in a proportion of from 0.1 to 10, preferably 0.2 to 2, wt.%, based upon the total weight of the lubricating oil composition provided the maximum phosphorus level is not exceeded. It may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohols or alkyl phenols with P_2S_5 and then neutralizing the DDPA formed with an appropriate metal, especially a zinc, compound. The dihydrocarbyl dithiophosphates may be made from mixed DDPA which in turn may be made from mixed alcohols.

Alternatively, individual dihydrocarbyl dithiophosphates may be made and subsequently mixed.

For certain uses, it may be advantageous to make the DDPA from either primary or secondary alcohols, or a mixture of primary and secondary alcohols. At least 50 mole % of the alcohols used to introduce hydrocarbyl groups into the dithiophosphoric acids are advantageously secondary alcohols. Thus the dihydrocarbyl dithiophosphoric acid may be made by reacting mixtures of primary and secondary alcohols. Alternatively, individual dithiophosphoric acids may be prepared with the hydrocarbyl groups on one secondary and the hydrocarbyl groups on the other primary. To make the metal compound any basic or neutral compound, especially a zinc compound, may be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to use of an excess of the basic zinc compound in the neutralization reaction.

The preferred zinc dihydrocarbyl dithiophosphates are oil soluble salts of dihydrocarbyl dithiophosphoric acids represented by the general formula $[(RO)(R^1O)P(S)S]_2Zn$ wherein

R and R¹ which may be the same or different are hydrocarbyl radicals containing from 1 to 18, preferably 2 to 12, carbon atoms. Examples of such radicals are alkyl, alkenyl, aryl, aralkyl, alkaryl and cycloaliphatic radicals, optionally substituted, provided the essentially hydrocarbyl nature is retained. Particularly preferred as R and R¹ groups are alkyl groups of 2 to 8 carbon atoms. The radicals may accordingly be, for example, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl, amyl, n-hexyl, i-hexyl, n-octyl, i-octyl, 2-ethylhexyl, nonyl, decyl, dodecyl, octadecyl, phenyl, butylphenyl, methylcyclopentyl, cyclohexyl, propenyl, butenyl, and 2-hydroxy-4-methylpentyl. In order to obtain oil solubility, the total number of carbon atoms (i.e. R and R¹) in the dithiophosphoric acid is advantageously at least 5.

15 The zinc dihydrocarbyl dithiophosphate is advantageously a zinc dialkyl dithiophosphate.

As indicated above, it is in accordance with the present invention to employ either copper compounds or molybdenum compounds in the composition. It is preferred, however, to employ both molybdenum compounds and copper compounds, and it is within the scope of the invention to employ mixtures of one or more copper compounds and one or more molybdenum compounds.

The copper and molybdenum are both present in oil-soluble form though they may be added in oil-insoluble form provided that in the final composition they are in oil-soluble form. The term "oil-soluble form" does not require solubility in oil in all proportions; rather the component is in oil-soluble form if it is soluble or colloïdally dispersible to an extent sufficient to have its intended effect in the environment where the lubricant is to be employed. Oil-soluble form may be achieved by resort to solubility aids. Inclusion of further additives may also promote the solution or dispersion of the component.

The amount of added copper in the compositions of the invention is preferably at least 2 ppm by weight of elemental copper. The amount of added copper advantageously does not exceed 500 ppm, and preferably does not exceed 200 ppm.

- 5 Especially advantageous compositions have copper in the range of from 2 to 100 ppm, preferably 50 to 100 ppm and especially about 80 ppm.

The term "added copper" is intended to exclude copper present in the oil as a result of accumulation of copper in
10 the oil during use, for example, as the result of wear or corrosion of copper-containing parts.

The added copper is advantageously in the form of an oil-soluble copper compound. The copper compound may be in cuprous or, preferably, cupric form. Examples of suitable
15 oil-soluble copper compounds include the oil-soluble copper compounds disclosed in EP-A- Nos. 24 146, 280 579 and 280 580, the disclosures of all of which are incorporated herein by reference. For example, the added copper may be blended into the oil as an oil-soluble copper salt of a synthetic or
20 natural carboxylic acid. Examples of carboxylic acids from which suitable copper salts may be derived include C₂ to C₂₂ saturated carboxylic, especially fatty, acids (e.g., acetic, stearic and palmitic acids), unsaturated acids (e.g., oleic acid), branched carboxylic acids (e.g., naphthenic acids of
25 molecular weight of from 200 to 500, neodecanoic acid and 2-ethylhexanoic acid), and alkyl- or alkenyl-substituted dicarboxylic acids (e.g., alkenyl-substituted succinic acids, for example, octadecenyl, dodecenyl and polyisobutenyl succinic acids). In some cases, suitable compounds may be
30 derived from an acid anhydride, for example, from a substituted succinic anhydride. The preferred acids are polyalkenyl succinic acids in which the alkenyl group has a number average molecular weight (Mn) greater than 700. The

alkenyl group desirably has a Mn from 900 to 1,400, and up to 2,500, with a Mn of about 950 being most preferred.

The added copper may be a copper dithiocarbamate of the general formula $(RR^1NCSS)_mCu$ or a copper dithiophosphate of the general formula $[(RO)(R^1O)P(S)S]_mCu$, where "m" is 1 or 2 and each of R and R^1 , which may be the same or different, represents a hydrocarbyl radical containing 1 to 18, preferably 2 to 12, carbon atoms, for example, an alkyl, alkenyl, aryl, aralkyl, alkaryl, or cycloalkyl radical. If a copper DDP is used, its phosphorus content must be taken into account; such compounds are accordingly not preferred. Other copper- and sulphur-containing compounds, for example, copper mercaptides, xanthates and thioxanthates, are also suitable, as are copper sulphonates, phenates (optionally sulphurized) and acetylacetonates.

Other copper compounds which may be used are overbased materials that contain copper. Examples of such compounds, and of processes for their preparation, are given in U.S. Patent No. 4 664 822 and EP-A-425 367, the disclosures of both of which are incorporated herein by reference. In the preparative processes described in the U.S. specification, the copper is used in an essentially oil-insoluble form, for example as the chloride, sulphate or C_1 to C_6 carboxylate, but in the overbased product the copper is incorporated into a colloiddally dispersed material in such a way that the product can act as an antioxidant for a lubricating composition. The European specification describes the use of copper C_7 to C_{10} carboxylates which are partially soluble in hydrocarbons so that in the overbased product they are situated at the interface of the base oil and colloiddally dispersed micelles.

If molybdenum is present, the composition advantageously contains at least 2 ppm of elemental molybdenum by weight. The proportion is advantageously at most 500 ppm, and

preferably at most 400 ppm. Especially preferred compositions contain from 50 to 350 ppm, especially about 250 ppm.

The molybdenum may be used in any available oxidation state. The molybdenum may be present as a cation, but this is
5 not essential. Thus, for example, molybdenum-containing complexes may be used.

Examples of molybdenum compounds which may be used include the molybdenum salts of inorganic and organic acids (see, for example, U.S. Patent No. 4 705 641), particularly
10 molybdenum salts of monocarboxylic acids having from 1 to 50, preferably 8 to 18, carbon atoms, for example, molybdenum octanoate (preferably 2-ethylhexanoate), naphthenate or stearate; the reaction product of molybdenum trioxide, molybdic acid or an alkali metal salt thereof (or the
15 reaction product of such a molybdenum compound and a reducing agent) and a secondary amine having hydrocarbon groups having 6 to 24 carbon atoms (see EP-A-205 165); overbased molybdenum-containing complexes as disclosed in EP-A-404 650, molybdenum dithiocarbamates and, less preferred because of
20 their phosphorus content, molybdenum dithiophosphates; oil-soluble molybdenum compounds as disclosed in U.S. Patents Nos. 4 995 996 and 4 966 719, particularly the molybdenum xanthates and thioxanthates described in those specifications; and oil-soluble molybdenum and sulphur-
25 containing complexes. Specific examples of molybdenum- and sulphur-containing complexes are those prepared by reacting an acidic molybdenum compound with a basic nitrogen-containing substance and then with a sulphur source (see, for example, GB-A-2 097 422), and those prepared by reacting a
30 triglyceride with a basic nitrogen compound to form a reaction product, reacting the reaction product with an acidic molybdenum compound to form an intermediate reaction product, and reacting the intermediate reaction product with a sulphur-containing compound (see, for example,

GB-A-2 220 954). Other examples of molybdenum compounds are described in co-pending International Patent Application No. PCT/IB97/01656 and comprise a trinuclear molybdenum core, optionally containing non-metallic atoms consisting wholly or partly of sulphur, and bonded thereto ligands capable of rendering the compound oil-soluble or oil-dispersible. The compounds may be represented by the general formula $\text{Mo}_3\text{S}_k\text{L}_p$, wherein

- L represents a ligand for example dithiocarbamate
p is in the range from 1 to 4 and
k is at least 4, especially 4 to 10, preferably 4 to 7.

The disclosures of all the specifications referred to in this paragraph are incorporated herein by reference.

- The mass ratio of added copper to molybdenum if both are present is advantageously in the range of from 10:1 to 1:10, preferably 3:1 to 1:3; and especially 2:1 to 1:2.

Further additives may be incorporated in the composition to enable it to meet particular requirements. Examples of additives which may be included are viscosity index improvers, corrosion inhibitors, detergents, metal rust inhibitors, pour point depressants, anti-foaming agents and other dispersants, anti-wear agents, oxidation inhibitors or antioxidants, and friction modifiers.

- Viscosity index improvers (or viscosity modifiers) impart high and low temperature operability to a lubricating oil and permit it to remain shear stable at elevated temperatures and also exhibit acceptable viscosity or fluidity at low temperatures. Suitable compounds for use as viscosity modifiers are generally high molecular weight hydrocarbon polymers, including polyesters, and viscosity index improver dispersants, which function as dispersants as well as viscosity index improvers. Oil-soluble viscosity modifying polymers generally have weight average molecular

weights of from about 10,000 to 1,000,000, preferably 20,000 to 500,000, as determined by gel permeation chromatography or light scattering methods.

Corrosion inhibitors reduce the degradation of metallic parts contacted by the lubricating oil composition. Thiadiazoles, for example those disclosed in US Patents Nos. 2 719 125, 2 719 126 and 3 087 932, are examples of corrosion inhibitors for lubricating oils.

Oxidation inhibitors, or antioxidants, reduce the tendency of mineral oils to deteriorate in service, evidence of such deterioration being, for example, the production of varnish-like deposits on metal surfaces and of sludge, and viscosity increase. Suitable oxidation inhibitors include sulphurized alkyl phenols and alkali or alkaline earth metal salts thereof; diphenylamines; phenyl-naphthylamines; and phosphosulphurized or sulphurized hydrocarbons.

Friction modifiers and fuel economy agents which are compatible with the other ingredients of the final oil may also be included. Examples of such materials are glyceryl monoesters of higher fatty acids, esters of long chain polycarboxylic acids with diols, and oxazoline compounds.

A viscosity index improver dispersant functions both as a viscosity index improver and as a dispersant. Examples of viscosity index improver dispersants suitable for use in lubricating compositions include reaction products of amines, for example polyamines, with a hydrocarbyl-substituted mono- or dicarboxylic acid in which the hydrocarbyl substituent comprises a chain of sufficient length to impart viscosity index improving properties to the compounds.

Detergents and metal rust inhibitors include the metal salts, which may be overbased, of sulphonic acids, alkyl phenols, sulphurized alkyl phenols, alkyl salicylic acids, thiophosphonic acids, naphthenic acids, and other oil-soluble mono- and dicarboxylic acids. Representative examples of

detergents/rust inhibitors, and their methods of preparation, are given in EP-A-208 560.

Pour point depressants, otherwise known as lube oil flow improvers, lower the minimum temperature at which the fluid will flow or can be poured. Such additives are well known. Foam control may be provided by an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

Some of the above-mentioned additives may provide a multiplicity of effects; thus for example, a single additive may act as a dispersant-oxidation inhibitor. This approach is well known and need not be further elaborated herein.

When lubricating compositions contain one or more of the above-mentioned additives, each additive is typically blended into the base stock in an amount which enables the additive to provide its desired function. Representative effective amounts of additives, including those essential to the invention, when used in crankcase lubricants, are as follows:

Additive	Mass % a.i.* (Broad)	Mass % a.i.* (Preferred)
Viscosity Modifier	0.01-6	0.01-4
Corrosion Inhibitor	0.01-5	0.01-1.5
Oxidation Inhibitor	0.01-5	0.01-1.5
Friction Modifier	0.01-5	0.01-1.5
Dispersant	0.1-20	0.1 -8
Detergents/rust inhibitors	0.01-6	0.01-3
Anti-wear Agent	0.01-6	0.01-4
Pour Point Depressant	0.01-5	0.01-1.5
Anti-Foaming Agent	0.001-3	0.001-0.15
Mineral or Synthetic Base Stock	Balance	Balance

* Mass % active ingredient based on the final oil.

It will be understood that the various components of the composition, the essential components as well as the optional and customary components, may react under the conditions of formulation, storage, or use, and that the invention also
5 provides the product obtainable or obtained as a result of any such reaction.

The invention also provides the use, in a crankcase lubricant, of a dispersant comprising a hydrocarbon polymer carrying a functional group, the polymer comprising monomeric
10 units derived from ethylene and from at least one α -olefin having from 3 to 16 carbon atoms, ethylene-derived units representing from 1 to 50% by weight of the polymer, the number average molecular weight being from 1500 to 10000, and at least 30% of the polymer chains having terminal
15 ethenylidene unsaturation before reaction to add the functional group, to improve fuel economy.

The invention further provides the use, in a crankcase lubricant containing at most 0.1% by weight of phosphorus, of a dispersant as defined above, a copper-containing compound
20 or a molybdenum-containing compound, to improve fuel economy while maintaining wear and oxidation resistance. Advantageously, the lubricant comprises both copper and molybdenum compounds.

The invention further provides an additive concentrate
25 comprising a dispersant as defined above, a copper-containing compound and/or a molybdenum-containing compound and a metal dihydrocarbyl dithiophosphate, and an oil or a solvent miscible with an oil, the proportions of the components being such that when the concentrate is incorporated in a lubricant
30 composition at a treat rate sufficient for the specified active components to carry out their functions effectively the proportion of phosphorus is at most 0.1% by weight of the lubricant composition. The concentrate advantageously

contains the specified active components in a proportion of from 5 to 95%, preferably 50 to 80%, by weight.

The invention further provides a method of lubricating an internal combustion engine, which comprises supplying to
5 the engine a lubricating composition according to the invention. Advantageously the engine is a spark-ignited engine.

The following examples, in which all parts and percentages are by weight unless indicated otherwise,
10 illustrate the invention.

In the examples, various tests were carried out. In the first test series fuel consumption using different lubricating oils was tested in a 2 litre Mercedes-Benz M111 16 valve DOHC gasoline engine.

15 In these tests, the engine was run continuously, oil changes being carried out using a "flying flush" technique. Each candidate oil was tested for 18 hours, six cyclic and steady states being measured, a reference oil being tested for 5 hours, over one cyclic and two steady states, the
20 engine being run for one hour with flushing oil after the reference oil test, enabling one candidate oil to be tested per day. Fuel consumption, expressed as Brake Specific Fuel Consumption (BSFC) in g/kW.h was recorded three times at each of three different temperatures, and the three records for
25 each temperature averaged. In the second test series, the high frequency reciprocating rig (HFRR) test, the coefficient of boundary friction is measured.

In the third test series, the "SMIRA" test, wear measurements are made on a single cam and tappet motored rig
30 (based on the MIRA rig developed by the Motor Industries Research Association (UK)). Wear is determined by measuring the reduction in width of a Vickers hardness indentation made in the centre of the tappet. Measurements are made after running the rig at three sets of temperature/speed

combinations: 40°C/250 rpm; 65°C/1500 rpm and 120°C/1500 rpm.

The fourth test series is a bench bulk oil oxidation test. Air is blown through the test sample at a fixed rate while the sample temperature is held at 165°C. An oxidation catalyst, a soluble iron salt, is added at the beginning of the test. Samples are withdrawn at regular intervals and their viscosity is measured using a HAALE viscometer. The degree of oxidation is measured as a percentage viscosity increase, relating the viscosity of the oxidized sample to the original viscosity of the sample.

Examples 1 and 2

In these examples, the fuel consumption, as measured by the M111 engine test, with the engine lubricated by a composition according to the invention, in which the dispersant was based on an ethylene- α -olefin polymer backbone, was compared with the fuel consumption of the engine when lubricated by a high quality commercial composition.

Each composition contained overbased magnesium and neutral calcium sulphonates, calcium phenate, PIBSA, ZDDP, nonylphenylamine antioxidant, demulsifier and antifoam.

The Example 1 composition contained as dispersant 19.2% by weight active ingredient of an ethylene/butene copolymer (45% by weight ethylene, molecular weight 1500, at least 30% terminal ethenylidene unsaturation) carboxylated by the Koch reaction and subsequently treated with polyamine (EBCO/PAM). The dispersant of Example 2, used at the same treat rate, was similar, except that the ethylene/butene copolymer contained 35% by weight ethylene rather than 45%. Comparison Example A composition contained as dispersant 24% by weight active ingredient of a polyisobutylenesuccinimide (PIBSAPAM PIB molecular weight 2250).

The fuel consumption of the engine using the Examples 1 and 2 and Comparison Example A lubricants was compared with that using a reference oil in accordance with the M111 engine test. The results, in terms of their respective Effective
5 Fuel Economy Indices (EFEI) were as follows:

Lubricant	EFEI
Example 1	1.2
Example 2	1.4
Example A	0.8

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The results show that an improvement in fuel economy results from the use of the dispersants according to the invention, the improvement with the 35% ethylene content polymer being more marked than that with the 45% ethylene
15 material.

Examples 3 to 10

By measuring the coefficient of friction in the HFRR test, a prediction of fuel economy is obtained. In these
20 examples, a series of lubricants was tested at various temperatures to evaluate the effects of (a) dispersant (ethylene-butene copolymer vs PIB backbone) (b) reduction in phosphorus content (c) addition of copper (d) addition of molybdenum and (e) variation in hydrocarbyl group in ZDDP.

25 All formulations contained 0.5% nonyl phenyl sulphide, 1.2% overbased magnesium and 0.5% neutral calcium sulphonates, 0.35% nonyldiphenylamine and small proportions of antifoam and demulsifier. The compositions of the comparative examples (Examples B to J) contained 6% PIBSAPAM,
30 the compositions according to the invention (Examples 3 to 10) contained 4.8% borated carboxylated ethylene/butene (molecular weight 1500, 45% ethylene, at least 30% terminal ethenylidene unsaturation) polyamide. All examples contained ZDDP's, either at a level to give a 0.09% loading of

phosphorus (Examples 4, 6, 8, 10, C, E, G and J) or at a level to give a 0.05% loading (Examples 3, 5, 7, 9, B, D, F and H). Examples 4, 5, 7, 10, B, E, G and H contained a ZDDP with primary hydrocarbyl groups, while the ZDDP's of Examples 3, 6, 8, 9, C, D, F and J contained secondary hydrocarbyl groups.

Examples 3, 4, 7, 8, B, C, F and G contained no molybdenum, while Examples 5, 6, 9, 10, D, E, H and J contained a molybdenum dithiocarbamate at a level sufficient to give a molybdenum loading of 240 ppm. Examples 3 to 6 and B to E contained no copper, while Examples 7 to 10 and F to J contained CuPIBSA at a level sufficient to give a copper loading of 80 ppm.

The HFRR test, measuring the coefficient of boundary friction at three of the different temperatures at which tests were carried out, gave the following results:

Example	Temperature		
	40°C	80°C	140°C
3	0.127	0.133	0.135
4	0.122	0.133	0.135
5 Mo	0.122	0.139	0.134
6 Mo	0.124	0.132	0.129
7 Cu	0.118	0.126	0.128
8 Cu	0.121	0.143	0.129
9 Mo, Cu	0.121	0.132	0.121
10 Mo, Cu	0.122	0.133	0.137
B	0.126	0.134	0.139
C	0.119	0.149	0.145
D Mo	0.131	0.136	0.138
E Mo	0.129	0.139	0.145
F Cu	0.124	0.140	0.137
G Cu	0.121	0.134	0.144
H Mo, Cu	0.126	0.139	0.144
J Mo, Cu	0.130	0.124	0.125

5

Cumulative results are obtained as follows:

To evaluate the effects of changing dispersant at a given temperature the coefficients of friction of examples according to the invention are summed, as are those of the comparative examples, and the difference between those numbers is divided by 8, the number of examples of each. A negative number is an improvement. A similar procedure is adopted to evaluate the other variables.

This is in accordance with standard analysis of factorial design experiments as described for example in "Statistical Design and Analysis of Experiments" by Robert L.

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Mason, Richard F. Gunst and James L. Hesso, published by John Wiley (1989); and "Statistics for Experiments: An introduction to Design, Data Analysis and Model Building" by Box, Hunter and Hunter, published by John Wiley (1978).

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	40°C	80°C	140°C
Invention vs PIBSAPAM	-0.0036	-0.0030	-0.0075
0.05% P vs 0.09% P	0.0009	-0.001	-0.0016
240 ppm Mo vs 0 Mo	0.0003	-0.0023	-0.0024
80 ppm Cu vs 0 Cu	0.0021	-0.0030	0.0044
Primary vs Secondary ZDDP	-0.0014	-0.0015	0.0059

The tests were also carried out at other temperatures (60°C, 100°C and 120°C); these showed cumulative comparisons
10 between dispersant of the invention and PIBSAPAM of -0.0027, -0.0055, and -0.0075. The results confirm that replacement of the PIBSAPAM dispersant by the ethylene-propylene copolymer based material results in a friction reduction and hence improvement in fuel economy at all operating
15 temperatures.

Example 11

The formulations of Examples 3 to 10 and comparative Examples B and C were subjected to the SMIRA tests to
20 ascertain the effect of replacing a PIBSAPAM dispersant with the dispersant of the invention. The results show that, in the absence of both copper and molybdenum, there is a decrease in wear-protection; this can be compensated by the

presence of either metal, and preferably both. The figures given below are the sums of the wear, in microns, measured at three temperatures, 40°C, 65°C, and 120°C, for the compositions shown. The following compositions contain no
5 copper or molybdenum.

	Composition	Wear, μm
	B	26.570
	C	11.284
10	Mean of B and C,	18.927
	3	17.285
	4	27.284
	Mean of 3 and 4,	22.285

15 These results show that replacing the PIBSAPAM with the dispersant of the invention increases wear, as does the reduction in phosphorus content.

The following compositions according to the invention show how copper and molybdenum compensate.

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Composition	Wear μm	Means
5 Mo	15.427	
6 Mo	16.714	5 and 6: 16.07
7 Cu	17.999	
8 Cu	9.570	7 and 8: 13.78
9 Cu + Mo	13.570	
10 Cu + Mo	11.998	9 and 10: 12.78

Example 12

The formulations of Examples 3 to 10 and B and C were subject to the ERCOT bench oxidation tests to ascertain the
25 effect of replacing PIBSAPAM with the dispersant of the invention. The extent of oxidation as measured by viscosity

increase after 16 hours at 165°C for compositions without copper or molybdenum is as follows:

Composition	Oxidation after	
	16 hours	60 hours
B	49.10	975.27
C	6.27	439.07
3	7.35	1060.54
4	16.63	1102.40

5 It is apparent from the above table that the lubricant compositions containing the PIBSAPAM dispersant (B and C) are less prone to oxidation than those containing EBCO/PAM dispersant (3 and 4). The extent of oxidation for compositions with one or both of copper and molybdenum, i.e.,
 10 compositions of the invention, is as follows, which shows how copper and/or molybdenum compensate in the sense of giving rise to improved oxidation control in the EBCO/PAM dispersant-containing compositions.

Composition	Oxidation after	
	16 hours	60 hours
5	1.38	25.89
6	0.00	31.18
7	1.92	216.15
8	3.31	38.60
9	-0.58	15.38
10	0.00	20.08

CLAIMS

1. A lubricant composition comprising a lubricating base stock, a dispersant, a metal dihydrocarbyl dithiophosphate, and either a copper-containing compound or a molybdenum-containing compound, the composition comprising at most 0.1% by weight of phosphorus, and the dispersant comprising a hydrocarbon polymer carrying a functional group, the polymer comprising monomeric units derived from ethylene and from at least one α -olefin having from 3 to 16 carbon atoms, ethylene-derived units representing from 1 to 50% by weight of the polymer, the number average molecular weight of the polymer being from 1500 to 10000, and at least 30% of the polymer chains having terminal ethenylidene unsaturation before reaction to add the functional group.

2. A composition as claimed in claim 1, wherein the phosphorus content is at most 0.08% by weight.

3. A composition as claimed in claim 1, wherein the phosphorus content is at most 0.05% by weight.

4. A composition as claimed in any one of claims 1 to 3, wherein the α -olefin from which the polymer is derived is propene or butene.

5. A composition as claimed in any one of claims 1 to 4, wherein the ethylene-derived content of the polymer is from 15 to 50% by weight.

6. A composition as claimed in any one of claims 1 to 5, wherein the molecular weight of the polymer is 1500 to 4500.

7. A composition as claimed in any one of claims 1 to 6, wherein at least 75% of the polymer chains have terminal ethenylidene unsaturation.
- 5 8. A composition as claimed in any one of claims 1 to 7, wherein functionality is provided by carboxylation at an ethylenic bond of the polymer and reaction of the carboxyl group with a nucleophile.
- 10 9. A composition as claimed in claim 8, wherein the carboxylation is effected by the Koch reaction.
10. A composition as claimed in claim 8 or 9, wherein the nucleophile is an amine.
- 15 11. A composition as claimed in claim 10, wherein the amine is a polyamine.
12. A composition as claimed in claim 11, wherein the
20 polyamine is of the formula
- $$\text{NH}_2(\text{alkylene-NA})_n\text{alkyleneNH}_2$$
- wherein A represents hydrogen or an alkyl group and n has an
25 average value of at least three.
13. A composition as claimed in claim 12, wherein the polyamine is a polyethyleneamine having an average of 5 to 8 nitrogen atoms.
- 30 14. A composition as claimed in any one of claims 1 to 13, wherein the dispersant is a post-treated dispersant.

15. A composition as claimed in any one of claims 1 to 14, wherein the dithiophosphate is a zinc dihydrocarbyl dithiophosphate.

5 16. A composition as claimed in any one of claims 1 to 15, which contains copper, and wherein the copper is present as a copper PIBSA.

10 17. A composition as claimed in any one of claims 1 to 16, which contains copper, and wherein the copper is present in a proportion within the range of 2 to 500 ppm.

15 18. A composition as claimed in any one of claims 1 to 15, which contains molybdenum, and wherein the molybdenum is present as a dithiocarbamate.

19. A composition as claimed in any one of claims 1 to 15 or 18, which contains molybdenum, and wherein the molybdenum is present in a proportion within the range of from 2 to 500
20 ppm.

20. A composition as claimed in any one of claims 1 to 19, which contains both copper and molybdenum.

25 21. A composition as claimed in any one of claims 1 to 20, which also comprises one or more of a dispersant, corrosion inhibitor, friction modifier, rust inhibitor, viscosity modifier, pour point depressant, antifoam, dispersant, antioxidant and antiwear agent other than one specified in a
30 preceding claim.

22. The use, in a crankcase lubricant, of a dispersant as defined in any one of claims 1 or 4 to 14, to improve fuel economy.

23. The use, in a crankcase lubricant containing at most 0.1% by weight of phosphorus, of a dispersant as defined in any one of claims 1 or 4 to 14, and a compound selected from
5 copper-containing and molybdenum-containing compounds, to improve fuel economy while maintaining wear and oxidation resistance.

24. The use as claimed in claim 23, wherein the lubricant
10 contains both copper and molybdenum.

25. An additive concentrate comprising a dispersant as defined in any one of claims 1 or 4 to 14, a metal dihydrocarbyl dithiophosphate, and a compound selected from
15 copper-containing compounds and molybdenum-containing compounds, and an oil or a solvent miscible with an oil, the proportions of the active components being such that when the concentrate is incorporated in a lubricant composition at a treat rate sufficient for the specified active components to
20 carry out their functions effectively the proportion of phosphorus is at most 0.1% by weight of the lubricant composition.

26. A method of lubricating an internal combustion engine,
25 which comprises supplying to the engine a lubricant composition as defined in any one of claims 1 to 21.

27. A lubricant composition substantially as described in any one of the numbered examples herein.

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28. Any new feature hereindescribed or any new combination of hereindescribed features.

INTERNATIONAL SEARCH REPORT

International Application No

PC1/EP 99/03311

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C10M141/10 C10M163/00 //(C10M141/10,129:95,133:52,135:18,
137:10),(C10M163/00,129:95,133:52,135:18,137:10,159:18,159:20),
C10N10:02,C10N10:12,C10N30:06,C10N40:25

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 0 353 935 A (EXXON CHEMICAL PATENTS INC) 7 February 1990 (1990-02-07) cited in the application	22
Y	page 25, line 26 - line 51 page 29, line 32 -page 30, line 56 page 31, line 15 - line 77 ----	1-21, 23-26
X	WO 96 16146 A (EXXON CHEMICAL PATENTS INC ;MACDONALD ISABEL PETRINA (GB); CLEVERL) 30 May 1996 (1996-05-30)	22
Y	page 22 -page 24; example 5; table 1 page 15, line 12 - line 26 page 16, line 6 - line 14 ----- -/--	1-21, 23-26

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/03311

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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